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**CRYOGENIC SAMPLING OF TURBINE ENGINE
EXHAUST**

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NOTICES

This progress report was submitted by personnel of the Bioenvironmental Analysis Branch, Environmental Sciences Division, USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas, under job order 7164-16-06.

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This technical report has been reviewed and is approved for publication.

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CRYOGENIC SAMPLING OF TURBINE ENGINE EXHAUST

INTRODUCTION

In order to obtain baseline data for assessing the biomedical impact of USAF aircraft operations, in May 1973, the USAF School of Aerospace Medicine (USAFSAM) initiated a cooperative study with the Air Force Aero Propulsion Laboratory (AFAPL), Wright-Patterson Air Force Base, Ohio. The objectives of the effort were to determine the hydrocarbon constituents of turbine engine exhaust, including (a) the relationship between fuel composition and exhaust composition; (b) the effects of smoke-abatement additives on exhaust composition; (c) the quality of hydrocarbon emissions which may affect an airfield and surrounding community environments.

Since hydrocarbon emissions are known to be lower from turbine engines than from either gasoline or diesel-powered internal combustion engines, improved sampling methodology to concentrate the organic exhaust constituents was needed to facilitate their detection and identification. For this purpose we used a multistage cryogenic trapping system developed by USAFSAM.

This report presents results of the initial cryotrap sampling tests which were conducted at AFAPL, in May 1973, primarily to establish feasibility of the cryogenic sampling technic. A T-56 combustor was used with two different fuels and additives.

EXPERIMENTAL

Sample Collection

Four samples of turbine engine exhaust were obtained from the AFAPL single-combustor test rig (Fig. 1). The test combustor was a T-56 type, commonly used in turboprop engines powering Air Force transport aircraft such as the C-130. Samples were obtained with the combustor simulating idle-power conditions. The fuels used were JP4 (sample 1), JP4 with a manganese additive (sample 2), JP5 (sample 3), and JP5 with an iron additive (sample 4). The manganese and iron compounds are classified as "antiknock" additives for intercombustion engine fuels and were undergoing smoke-abatement characterization in the subject tests. The manganese additive, methylcyclopentadienyl manganese tricarbonyl, was added to the neat JP4 fuel at a concentration of 100 ppm by weight. The iron additive, dicyclopentadienyl-iron (ferrocene), was used in JP5 at 100 ppm by weight. (Ferrocene has been used by the Navy for smoke abatement in their turbine engine test cells.)

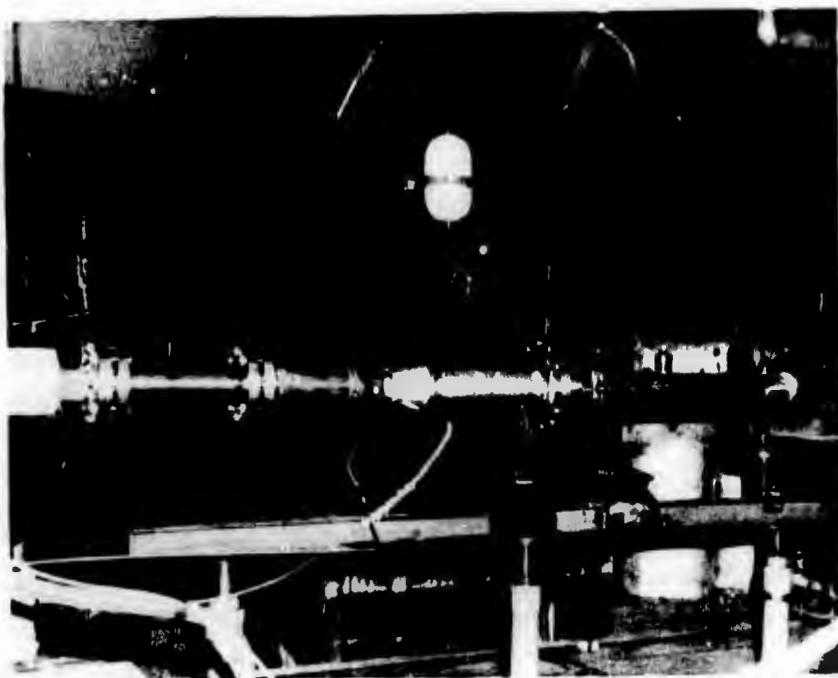


Figure 1. T-56 Combustor Test Rig (AFAPL).

Sampling was accomplished with a 6.4-mm (1/4-inch) stainless steel probe located in the combustor outlet. The hot exhaust gas was fed through approximately 7 meters of unheated 6.4-mm transfer line to the cryogenic trap system and also to a bank of instruments for analyzing carbon monoxide, nitrogen oxides, total hydrocarbons, and smoke. Sample flow to the cryotrap system was controlled at 500 cc/min at standardized conditions of 21.1°C and 760 mm Hg. The collection periods were 30 minutes (15 liters) for samples 1-3 and 60 minutes (30 liters) for sample 4.

Cryogenic sample collection was accomplished in a three-stage system (Fig. 2). The first stage was maintained at 0°C (ice water), the second at -78°C (crushed solid carbon dioxide), and the third at -175°C (liquid nitrogen). Sample flow was continuous through the three traps in series and was exhausted to ambient. Two unique features of the cryotrap system were a heated inlet to the -78°C trap to prevent ice formation, and a gaseous nitrogen flush in the -175°C trap matrix to prevent condensation of liquid oxygen. The trap vessels were 150-cc stainless steel cylinders (Whitey P/N HDF4-150-304).

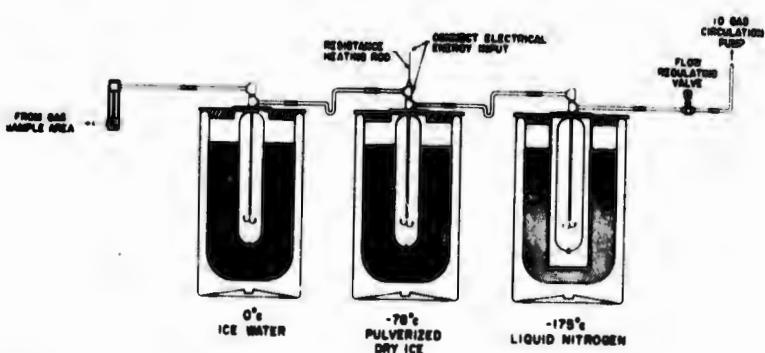


Figure 2. USAFSAM 3-stage cryogenic sampling system and gas flow path.

Exhaust Analysis

The cryotrap exhaust samples were qualitatively analyzed by a coupled gas chromatograph-mass spectrometer system (Dupont Model 21-491) and a dedicated data-processing and library-search computer (Dupont Model 21-094). Identification of individual compounds was based on spectra of 6000 individual compounds.*

*Stenhammar, E., A. Abrahamsson, and F. W. McLafferty. *Atlas of Mass Spectral Data (3 volumes)*. New York: Wiley-Interscience, 1969.

First, each trap cylinder was warmed to 150°C to revaporize trapped material and ensure a homogeneous sample. The sample was introduced into the chromatograph both by direct injection and by concentrated injection via cryogenic sample loop. In the direct method, the sample was expanded into a 2.9-cc preevacuated sample loop, equilibrated at room temperature, and flushed into the chromatograph with carrier gas. In the concentrated method, the sample cylinder was prepressurized (after warming) to 1460 mm Hg with ultrapure helium, and the resultant mixture discharged at 6 cc/min through a 2.9-cc sample loop maintained at -78°C with dry ice. Following sample collection, the loop was closed and heated to 150°C, and the sample flushed into chromatograph with carrier. The concentrated method of analysis amplified the chromatographic peaks to facilitate compound identification.

The coupled chromatograph (Varian Model 1400) was a single-column instrument equipped with a flame ionization detector (FID). The separation column was a 3-m stainless steel tube 1.6-mm-diameter packed with 100/120 mesh Porapak Q. The helium carrier gas had a flow rate of 30 cc/min.

The chromatographic run was temperature programmed according to the following schedule: initial isothermal at 0°C for 10 minutes, 6°C/min to 245°C, and terminal isothermal at 245°C for 30 minutes.

The chromatographic column effluent was split one-third to the flame ionization detector and two-thirds to the mass spectrometer via jet separator for sample enrichment. The mass spectrometer ionization chamber was maintained at 250°C, and the source pressure was 10⁻⁶ mmHg or less with the chromatographic effluent to the mass spectrometer. Further, with the mass spectrometer repetitively scanning at 2 seconds per decade, the data system was calibrated between mass-to-charge (m/e) 12 and 219. Data acquisition was done at 10 kHz with an ion threshold of 1.

Fuel Analysis

The neat JP4 and JP5 fuels were analyzed by the GC-MS-data system with the same column and conditions as for the exhaust samples. The sample was injected to the chromatograph from the 2.9-cc gas sample loop following vaporization (at 150°C) of 1-5 microliters of the liquid fuel.

RESULTS AND DISCUSSION

Exhaust Composition

Table 1 lists the hydrocarbon compounds found in T-56 combustor exhaust with the four different fuel samples used. The exhaust data

TABLE 1. EXHAUST HYDROCARBON COMPOUNDS

<u>COMPOUNDS/FUEL</u>	<u>JP4</u>	<u>JP4+Mn^a</u>	<u>JP5</u>	<u>JP5+Fe^b</u>
PARAFFINS				
Propane	2	1	1	3 x
3,4-Dimethylheptane	x			
n-Heptane	x			
1-Phenyl-2,4-dimethylpentane		x		
2,2,4-Trimethylpentane			x	
3-Methyloctane				x
2,4-Dimethylheptane				x
OLEFINS				
Propene	1 x	5	7 x	5 x
2-Methylpropene		x	x	x
2-Butene		x	x	x
Trimethylene oxide				x
Propylene oxide		x		
2-Pentene				x
1-Pentene			x	
4-Methyl-1-hexene		x	x	
1-Hexene			x	
1-Phenyl-2-butene			x	
4-Phenyl-1-butene		x		
NAPHTHENES	1	2 x	2	0
Cyclobutane			x	
Cyclopentane			x	
Cyclooctatetraene	x	x	x	
AROMATICS	5	5	5 x	6 x
Benzene	x	x		
(2-Methylpropenyl) Benzene	x	x		
Methylallylbenzene			x	
Isobutylbenzene			x	
Toluene	x	x	x	
Ethylbenzene	x			
Xylene				x
Styrene	x			x
1,2,3,4-Tetrahydronaphthalene		x	x	
O-Allyltoluene		x	x	
ACIDS	0	0	0	2 x x
Hydrozoic				
Phenol				
ALDEHYDES	5	8 x	6 x	10 x
Acetaldehyde				
Acrolein		x	x	x
Propanal	x	x	x	x
2-Butanal				x
Butanal	x	x	x	x
3-Methylbutanal	x	x	x	x
Isovaleraldehyde		x	x	x
2-Furfural				x
Hexanal	x	x	x	x
n-Heptanal	x	x	x	x
Benzaldehyde	x	x	x	x
ALCOHOLS	2	5 x	5 x	5 x
Methanol				
Ethanol		x	x	x
2-Methyl-2-propanol	x	x	x	x

^aMethylcyclopentadienyl manganese tricarbonyl^bDicyclopentadienyl iron (ferrocene)

TABLE 1. (CONTINUED)

<u>COMPOUNDS/FUEL</u>	<u>JP4</u>	<u>JP4+Mn^a</u>	<u>JP5</u>	<u>JP5+Fe^b</u>
3-Heptanol			x	
2,3-Dimethyl-2-pentanol			x	
3-Methyl-1-butanol		x		x
2-Butene-1-ol				
2,3-Dithiobutanol				x
Cyclohexanol	x	x		x
2-Ethyhexanol				x
 KETONES	<u>2</u>	<u>3</u>	<u>5</u>	
Acetone	x	x	x	x
Methyl vinyl ketone		x	x	x
Methyl ethyl ketone		x	x	x
Cyclopentanone				x
Methyl tert-butyl ketone	x	x	x	x
Isopropyl tert-butyl ketone			x	x
1-Indanone			x	
 ETHERS	<u>1</u>	<u>3</u>	<u>1</u>	<u>4</u>
Allyl vinyl ether			x	
Furan				x
Vinyl methyl ether		x		
Ethyl n-butyl ether				x
2,3-Epoxybutane		x		x
Ethyl vinyl ether		x		x
Tetrahydrofuran				x
Isobutyl vinyl ether				
Benzyl ether	x			
 ESTERS	<u>6</u>	<u>2</u>	<u>3</u>	<u>3</u>
Ethyl formate		x		x
Vinyl acrylate	x			
Vinyl propionate	x		x	
Methyl acetate				
Ethyl-a-hydroxyisobutyrate	x			
Vinyl formate	x			
Methyl methacrylate	x			x
Ethyl methacrylate				x
Butyl acetate		x	x	
Isobutyl acetate	x		x	
 SULFUR CONTAINING	<u>0</u>	<u>0</u>	<u>1</u>	<u>1</u>
Carbon disulfide			x	
n-Butyl mercaptan				x
 NITROGEN CONTAINING	<u>3</u>	<u>4</u>	<u>3</u>	<u>3</u>
Nitrous oxide	x			
2-Nitropropane			x	
Ethane nitrile	x	x	x	x
Diazoethane			x	x
Nitromethane	x	x	x	x
Propane nitrile		x		
Se Butyl isothiocyanate		x		
 CHLORINE CONTAINING	<u>4</u>	<u>4</u>	<u>6</u>	<u>4</u>
Chloromethane		x	x	
Di-chlorodifluoromethane (R-12)	x	x	x	x
Ethyl chloride			x	
Propionyl chloride			x	
Dichloromethane	x	x		x
Isoamyl chloride			x	
Trichloroethylene	x	x	x	x
Chlorobenzene				x
Tri-chlorotrifluoroethane (R-113)	x			

^aMethylcyclopentadienyl manganese tricarbonyl^bDicyclopentadienyl iron (ferrocene)

support two qualitative observations. One was that the heavier fuel, JP5, tended to produce a greater total number of exhaust compounds than did JP4 and the incremental constituents appeared as olefins, alcohols, and ketones. Qualitatively, 32 compounds were identified in exhaust from JP4 and 45 with JP5; 17 compounds were common to both fuels. Comparison of exhaust from these fuels showed JP5 with more compounds than JP4 in olefins (7 to 1) and in both alcohols and ketones (5 to 2 each). The other compound classifications remained essentially equal, with the exception of the esters which had fewer species in JP5 exhaust. The fact that approximately 50% of the organic exhaust constituents appeared as partially oxidized moieties (Table 1) indicated that the cryogenic trap samples provided a minimally altered reactive exhaust sample.

A second observation in the data was that adding a metal-based smoke-abatement additive to each neat fuel also resulted in more exhaust constituents. In this case increases common to both fuels appeared primarily as ethers and aldehydes. It is perhaps significant that ether formation was almost completely limited to additive-containing fuels.

An example of JP4 and JP5 fuel analysis is shown to indicate their differences (Fig. 3). This also illustrates the many types of hydrocarbons which may, when combusted, give a multiplicity of compounds. The dotted lines in the figure represent a 20-fold and 4-fold expansion of the JP4 and JP5 data. The fit, the degree of match to library spectra (based on 1000), is shown by the numbers in parentheses after the compound identification.

Efficacy of Exhaust Sampling

In this sampling study, cryogenic trapping of turbine engine exhaust hydrocarbons was not only feasible, but virtually mandatory, for collecting an adequate sample for analysis.

The paucity of detectable sample necessitated the second cryogenic trapping step (in the gas-chromatograph sample loop) for constituent identification and largely precluded any attempt at individual compound quantitation. A typical analysis of the concentrated JP5 exhaust sample is depicted in Figure 4. The dotted line in the 0° and -78° C traps represents a 10-fold expansion of the data. The approximate hydrocarbon concentration, calculated from trapped exhaust sample, was 0.47, 0.40, 0.38, and 0.24 ppm for samples 1-4 respectively. These estimates are based on benzene FID response and were obtained by integrating the total area under the gas chromatogram. The quantity of trapped hydrocarbon detection after double concentrations was 16, 14, 14, and 30 micrograms, for samples 1-4 respectively.

CONCLUSION

This study has shown the need for longer exhaust sampling periods to obtain sufficient material for quantitation. The amount of organic material collected from the exhaust gases was substantially less than expected, which was, in part, due to deposition of sample in the unheated transfer lines. The additional cryogenic transfer (at -78°C) prior to analysis proved useful for concentration purposes, but introduced a degree of uncertainty in the data owing to possible loss of lower boiling compounds. Future sampling studies (to be reported) have incorporated heated transfer lines and 90-minute sampling periods to overcome these deficiencies.

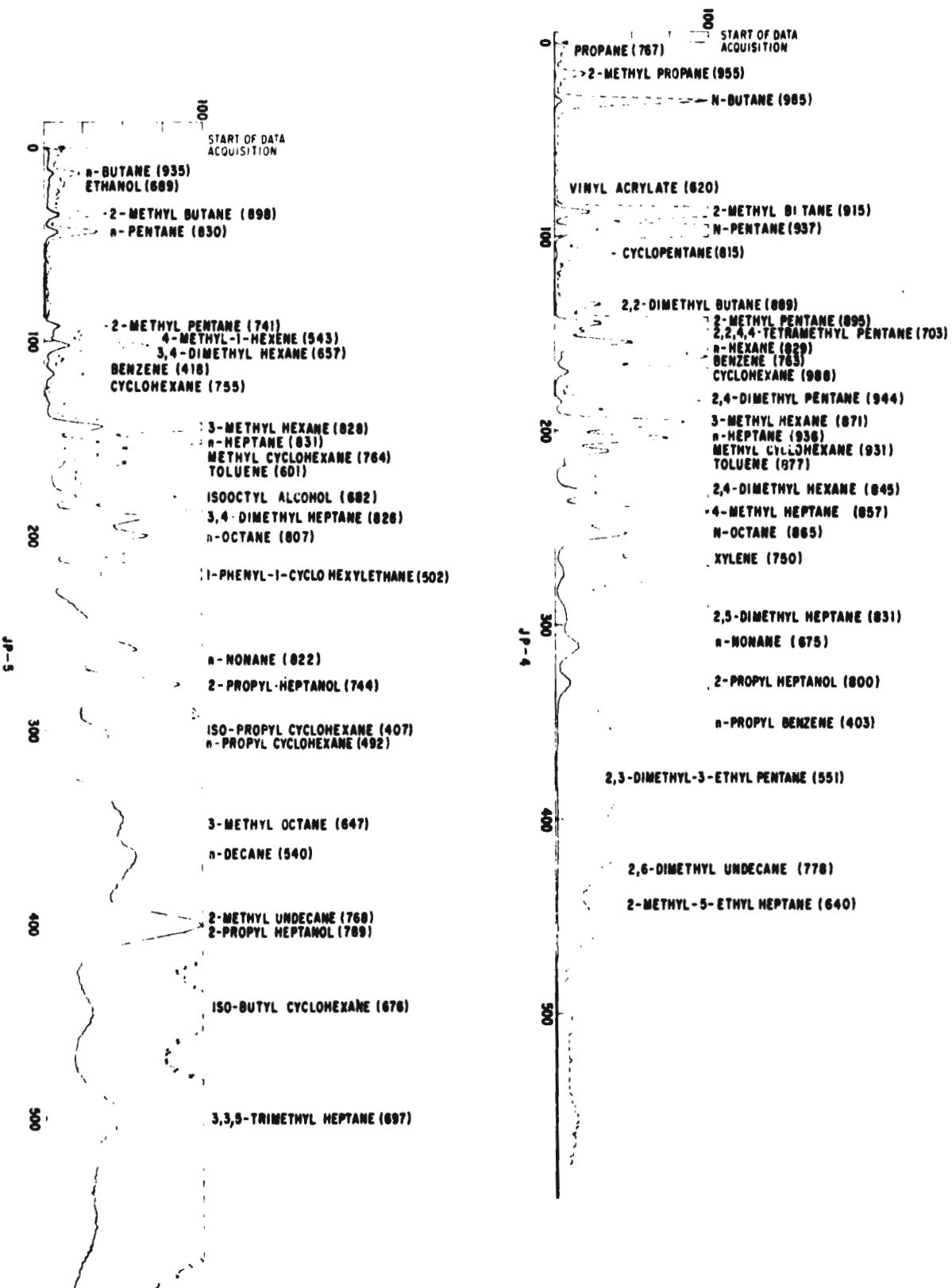


Figure 3. Mass chromatogram of JP4 and JP5.

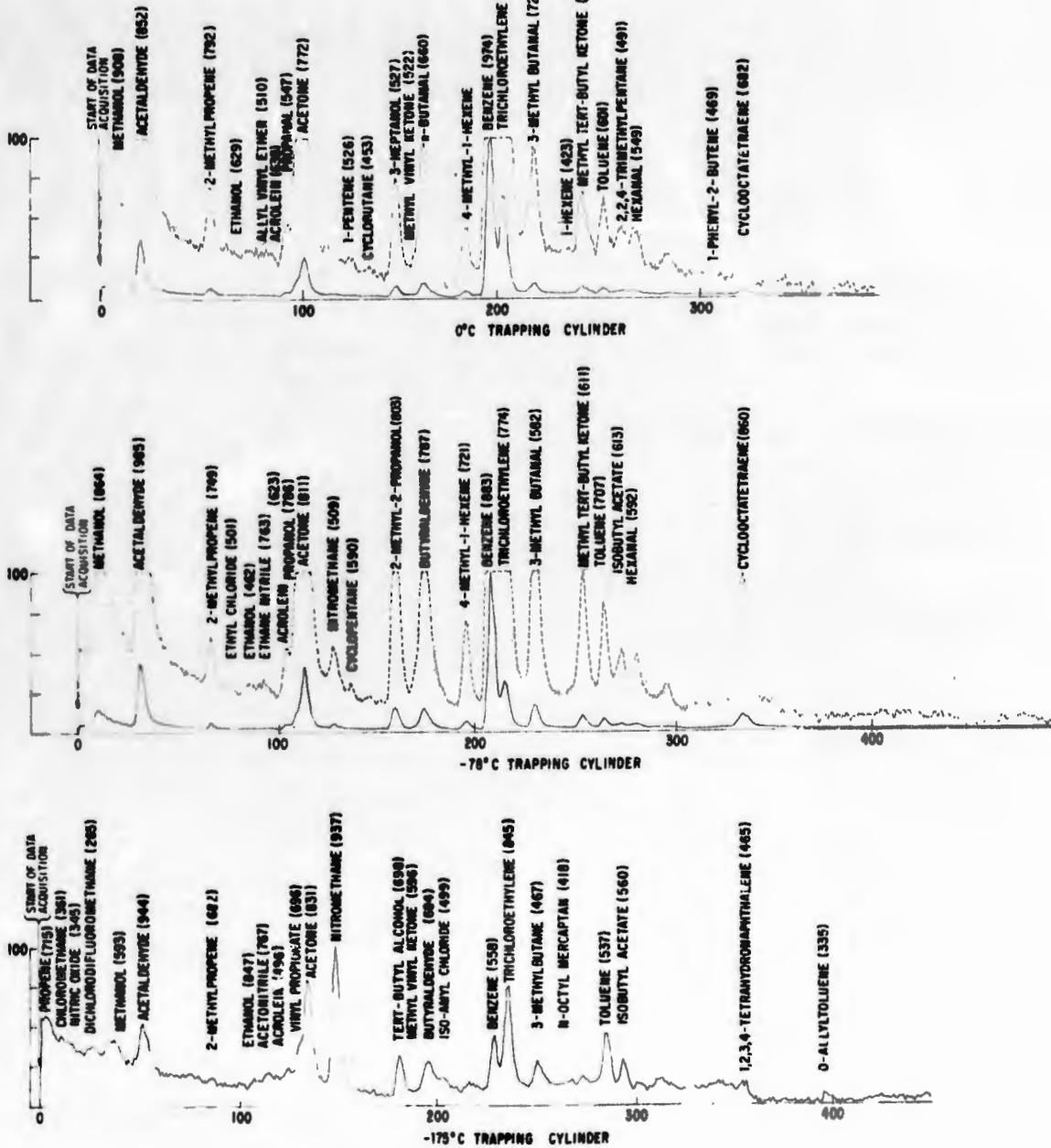


Figure 4. Mass chromatogram of turbine engine combustor exhaust sampled by 3-stage cryogenic trap and reconcentrated at -78° in GC sample loop.
Fuel was JP5.